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(54) A sustainedly vapor-releasing body for environmental control.

(57) The invention provides a sustained vapor-releasing body for emission of a gasifiable and diffusible substance capable of exhibiting an activity even in an extremely low concentration in the atmospheric air such as sex pheromones for insects and insecticides used for the pest control in agriculture and forestry, bactericides, perfumes and the like at a controlled rate of emission. The vapor-releasing body of the invention comprises a solid base particle shaped of a blend of an inert carrier material such as anhydrous silicic acid and the gasifiable active substance together with a binder and a coating layer on the surface of the solid base particle formed of a film-forming polymeric material such as a cellulose derivative including cellulose ethers, cellulose esters and cellulose ether esters. Incorporation of an inorganic powdery material into the coating layer further provides a means for controlling the rate of vapor emission from the body and easiness in the preparation thereof.

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A SUSTAINEDLY VAPOR-RELEASING BODY FOR  
ENVIRONMENTAL CONTROL

BACKGROUND OF THE INVENTION

5       The present invention relates to a sustainedly vapor-releasing body for environmental control or, more particularly, to a vapor-releasing body capable of emitting a vapor diffusible into and capable of exhibiting activities in the atmosphere at a controlled rate. The inventive vapor-releasing body is particularly useful as a perfume-dispenser and  
10       an emitter of a sex pheromone of noxious insects or pests to provide an efficient means for the extermination or control of the pests in the agriculture and forestry.

15       In connection with vaporizable or sublimatable substances diffusible into and capable of exhibiting activities in the atmosphere even in an extremely low concentration, such as a sex pheromone of insects and a perfume or deodorant, it is very important that the vapor of the active substance is emitted or released sustainedly at a controlled  
20       rate into the atmosphere over a length of time so that various attempts have been proposed for sustainedly controlling the rate of vapor-releasing of such substances. For example, insectan sex pheromones are shaped into a form like a solid  
25       medicament from which the vapor of the pheromone is emitted at a controlled rate to exhibit the desired effect sustainedly in the atmosphere.

A composition for the sustained release of the vapor of an insectan pheromone should satisfy several requirements including, for example:

- 5 (1) a constant or controlled rate of emission of the pheromone over a desired length of time;
  - (2) stability of the pheromone contained therein to cause loss thereof as small as possible;
  - (3) biodegradability of the components to cause no environmental pollution;
  - 10 (4) easiness of application thereof to actual fields; and
  - (5) easiness of preparation and inexpensiveness,
- while no prior art compositions or bodies hitherto developed can satisfy all of these requirements.

15 Various types of compositions and bodies for sustained release of pheromones have been proposed in the prior art including microcapsule-type ones by use of gelatin or polyamide resins disclosed in U.S. Patents 2,800,457, 2,800,458 and 3,577,515, film dispenser-type ones of multi-layered  
20 structure disclosed in A.C.S., volume 33, page 283 (1976), hollow fiber-type ones of capillaries having open ends disclosed in U.S. Patent 4,017,030 and sticking agents admixed with a pheromone compound. These prior art pheromone releasing compositions or bodies have their respective disadvantages  
25 and problems. For example, the problems in the microcapsule type ones are that gelatin has poor weathering resistance and polyamide resins are not biodegradable in

addition to the expensiveness. The film dispenser-type and hollow fiber-type ones have a deficiency that, in addition to the problem of the non-biodegradability of the materials forming the films or fibers, they must be distributed in the outdoor fields by use of a special distributor machine. The pheromone-admixed sticking agents are defective due to the difficulty in controlling the releasing velocity of the pheromone which is sometimes excessively large directly after application of the sticking agent while the releasing velocity rapidly decreases in the lapse of time consequently with unsatisfactorily short serviceable life. This deficiency is more remarkable in a hot weather as in summer.

Another important class of the compounds for which a means for sustainedly controlling the rate of vapor emission to the atmosphere is desired is perfumery since perfumes as well as deodorants are usually vaporizable and the pleasant effect obtained with a perfume is naturally transient because the effect is obtained only by the vapor of a perfume floating in the air in a trace concentration.

Various methods have been proposed for sustainedly obtaining the effect of a perfume without frequently repeating spraying of a liquid perfume including a method in which a solid base material such as a gum, silica gel, active charcoal and the like is impregnated with the perfume and emission of the perfume takes place from the thus perfume-

impregnated solid at room temperature or with heating, a method in which the perfume is contained and confined in a container having an opening with a limited small area so that the emission of the perfume to the atmospheric air takes place only through the opening of the limited size, a method in which a sublimatable substance is impregnated with the perfume and the emission of the perfume takes place along with the sublimation of the sublimatable substance, and others.

10

These conventional methods for the sustained release of perfumes are not always quite satisfactory, for example, because of the requirement for a specific device and unstable rate or insufficiently long duration of the perfume emission. In addition, these conventional methods are not applicable when a sustainedly perfume-releasing body in a particulate or granular form is desired to facilitate handling.

Recently, some proposals have been made for sustainedly controlling the emission of perfumes including a granular perfume-dispenser prepared by providing a coating film of a vapor-permeable cellulose derivative on the granules of an active alumina impregnated with a perfume (see, for example, Japanese Patent Publication 56-7423) and a perfumery tablet prepared by the adsorption of a perfume on a hygroscopic adsorbent followed by tableting and coating of the tablet with a polymeric coating material in such a thickness that the

25

perfume can be released to the atmosphere only when the tablet is heated (see, for example, Japanese Patent Kokai 53-69840). These methods are also not free from some problems that the rate of perfume releasing from the granular perfume dispenser is relatively large in the beginning stage of its use but rapidly decreases in the lapse of time not to provide good control of the releasing rate in addition to the relatively large loss of the perfume in the preparation of the perfumery tablet which is effective only when it is heated.

The above mentioned sex pheromones of insects and perfumes belong only to a part of typical classes of compounds gasifiable by vaporization or sublimation and diffusible into the atmosphere of which efficient means for sustained and controlled release of the vapor are desired including deodorants, insecticides, bactericides, pest repellents, fumigants and the like. All of the sustainedly vapor-releasing bodies for these substances should satisfy similar requirements to those in the insectan sex pheromones and perfumes while none of the prior art materials is quite satisfactory in all respects. Similarly to pheromones, for example, the biodegradability of the components to cause no environmental pollution and the easiness in the application to the fields are some of the essential conditions in the sustainedly vapor-releasing bodies for insecticides, bactericides and pest repellents used in forestry, agriculture and horticulture.

# SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a sustainedly vapor-releasing body capable of emitting a gasifiable and diffusible substance, such as an insectan sex pheromone and perfume, at a controlled rate without the problems and disadvantages in the above described prior art materials of vapor-releasing body.

The sustainedly vapor-releasing body of the present invention developed as a result of the extensive investigations continued by the inventors comprises a solid particle formed of a composition comprising a gasifiable and diffusible substance capable of exhibiting an activity when contained in the atmospheric air in an extremely low concentration, an inert carrier material for the gasifiable and diffusible substance and a binder and a coating layer on the surface of the solid particle formed of a polymeric material. In particular, the coating film of a polymeric material may contain an inorganic powdery material in a specified proportion to the polymeric base material.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The above described sustainedly vapor-releasing body of the present invention can satisfy all of the requirements for such materials described in (1) to (5) above. Moreover, it is a relatively easy matter to adequately control the velocity of emission of the active substance from the

inventive sustainedly vapor releasing body by the suitable selection and adjustment of the relative amounts of the inert carrier material and the binder, the particle size or surface area of the body and the thickness of the coating layer as well as by the incorporation of an inorganic powdery material into the coating layer. In addition, the sustainedly vapor-releasing body of the invention can be a tiny particle of any small size suitable for the preparation by a conventional method of granulation so that the particles can be distributed over the fields in the form of the granules as such or in the form of an aqueous suspension containing a spreading agent, according to need, by use of an ordinary distributor machine without consumption of a large manpower in the case of sex pheromones of insects, insecticides, bactericides and the like used in agriculture and horticulture. In the case of pheromone-containing vapor-releasing bodies, in particular, the invention provides a possibility of obtaining a more uniform distribution of the pheromone-emitting source over the field in the application for disturbing the intercommunication of insects with sustained release of the pheromone at a constant and controlled rate to achieve more efficient utilization of the pheromone. An additional advantage of the present invention is the degradability of the base materials used in the inventive vapor-releasing body after lapse of certain period of time without the danger of accumulation in nature to cause environmental pollution.

The active ingredient in the inventive sustainedly vapor-releasing body is a vaporizable and diffusible substance capable of exhibiting certain activity when it is gasified by vaporization or sublimation and contained in the atmospheric air even in an extremely low concentration. Examples of such a material are sex pheromones of insects, insecticides, bactericides, repellents, fumigating agents, perfumes and the like.

The above mentioned insectan pheromone belonging to an important class of the gasifiable and diffusible active substances is not particularly limited to a specific type but may be any one capable of exhibiting the desired activity to the species of the insects to be exterminated or controlled of the population. It is of course that the pheromone may be a single compound or a mixture of a plurality of active compounds. It is also optional that the pheromone is admixed with conventional additives such as a stabilizer typically represented by ultraviolet absorbers and antioxidants.

20

The perfume belonging to another important class of the active ingredients in the inventive sustainedly vapor-releasing body is also not limited to a specific one but any kinds of perfumes may be used in the invention including single perfumes and compounded perfumes. The perfume may of course be admixed with conventional additives such as a stabilizer typically represented by ultraviolet absorbers and

antioxidants.

The solid particle is formed of a composition comprising the gasifiable and diffusible active substance, an inert carrier material and a binder although the use of a binder largely depends on the nature of the inert carrier material. The material suitable as a carrier of the active substance such as insectan pheromones and perfumes should be inert to the active substance and have good capacity of adsorbing the active substance. Such an inert carrier material is exemplified by inorganic powdery materials such as anhydrous silicic acid, various kinds of silicates, talc and the like and organic powders such as polysaccharides, e.g. cellulose and starch, and derivatives thereof in a powdery form. The weight proportion of the active component to the inert carrier material of course depends on the type of the active component and the intended use of the inventive sustainedly vapor-releasing body but it is usually in the range from 1:0.3 to 1:10 or, preferably, from 1:0.3 to 1:3 when the active component is an insectan pheromone.

The binder may be selected from the group of polysaccharides such as starch, pullulan, xanthan gum and the like, derivatives of polysaccharide such as cellulose derivatives and synthetic polymers such as polyamides, polyesters, polyethers and vinylic polymers. It is advantageous to use a binder material having good miscibility or compatibility

with the active component such as the insectan pheromone and perfume.

The coating layer provided on the surface of the solid particles containing the gasifiable and diffusible active substance is formed of a film-forming polymeric material having an adequate permeability to the vapor of the gasifiable active substance contained in the solid particle such as those named above as the examples of the binder material. It is also important that the film-forming polymeric material for the coating layer has a good degradability by bacteria or enzymes so as not to be accumulated in nature without causing the problem of environmental pollution. The film-forming polymeric material should desirably be soluble in a solvent having a boiling point of 120 °C or below. These film-forming polymeric materials may be used either singly or as a combination of two kinds or more according to need provided that they have good compatibility with each other. In particular, the cellulose derivatives are exemplified by methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxyethyl methyl cellulose, hydroxypropyl methyl cellulose, ethyl cellulose, ethyl carboxymethyl cellulose, carboxymethyl cellulose and the like cellulose ethers, cellulose acetate, cellulose acetate phthalate and the like cellulose esters and hydroxypropyl methyl cellulose phthalate, hydroxypropyl methyl cellulose acetate succinate and the like cellulose ether esters.

These cellulose derivatives are very satisfactory as the coating material used in the inventive sustainedly vapor-releasing body because they have a good film-forming property to coat the solid particles with a film having an adequate permeability to the gasifiable and diffusible active substance to provide a means of controlling the rate of emission of the active substance into the atmospheric air. In addition, these cellulose derivatives are readily decomposed by bacteria or cellulase to be returned to the nature without causing the problem of environmental pollution.

When the cellulose derivative used for coating the solid particles impregnated with the gasifiable and diffusible active substance is insoluble in water having a value of pH at or in the vicinity of 7, the sustainedly vapor-releasing body of the invention is stable even in contact with water. When the cellulose derivative is soluble in water, on the other hand, the sustainedly vapor-releasing body of the invention can no longer be stable in contact with water. It is preferable in such a case, therefore, that the sustainedly vapor-releasing body coated with the cellulose derivative is subjected to a treatment for insolubilizing the cellulose derivative against water when the vapor-releasing body is expected to be used with a possibility of being brought into contact with water although such an insolubilizing treatment of the cellulose derivative is not important for the vapor-releasing body used without being brought into contact with

water. Generally, sustainedly vapor-releasing bodies for the emission of a sex pheromone of insects are used in an open field where the vapor-releasing bodies are frequently wet with rain or water sprinkling so that the insolubility of the cellulose derivative is very important in order to avoid dissolution of the coating film and disintegration of the body.

The coating film on the solid particles may not be formed of a single kind of the cellulose derivatives but it is optional to use two kinds or more of the cellulose derivatives in combination according to need to provide the coating film on the solid particles. It is also optional that the cellulose derivative is admixed with a wax-like material such as stearic acid which serves as a film-forming aid. The coating layer may be formed of a blend of the above mentioned film-forming organic polymer and an inorganic powdery material. Such an inorganic powdery material may be anhydrous silicic acid, various kinds of silicates, talc and the like and serve to further facilitate control of the releasing rate of the active substance contained in the solid particles. The amount of the inorganic powdery material in the coating layer should be 4 times by weight or less of the film-forming polymeric material.

25

A typical formulation of the inventive sustainedly vapor-releasing body is as follows, in which the amount of

each of the components is given in % by weight based on the total weight of the body.

Base particles:

5	Active ingredient	0.5 to 60 % by weight
	Stabilizer	0 to 6 % by weight
	Inert carrier	10 to 50 % by weight
	Binder	1 to 30 % by weight

Coating layer:

10	Film-forming polymer	5 to 50 % by weight
	Inorganic powder	0 to 30 % by weight

The above given formulation should of course be within the preferable limitations that the weight ratio of the active ingredient, e.g. insectan pheromone or perfume, to the inert carrier is in the range from 1:0.3 to 1:10, the weight ratio of the inert carrier to the binder is in the range from 1:0.1 to 1:3 and the weight ratio of the film-forming polymeric material to the inorganic powdery material is in the range from 1:0 to 1:4. When the active ingredient is an insectan pheromone, in particular, it is preferable that the content thereof is at least 11 % by weight. When the content of the active ingredient is lower than the above mentioned range, the rate of vapor emission thereof from the inventive body may be too low so that no sufficiently high activity of the active substance can be exhibited in the atmosphere. For example, the vapor-releasing body containing an insectan

pheromone in such a low content must be distributed in the field in an excessively large amount to cause an economical disadvantage and decreased adherence to the twigs of trees and the like when the vapor-releasing bodies are distributed by the aid of a spreading agent. Higher contents of the active ingredient over 60 % by weight is disadvantageous due to the increased vaporization loss in the course of the preparation of the inventive vapor-releasing body as well as due to the difficulty in the control of the rate of vapor emission.

The typical procedure for the preparation of the sustainedly vapor-releasing body of the invention is as follows.

In the first place, the active ingredient such as an insectan pheromone and perfume, inert carrier material and, if necessary, stabilizer for the active ingredient are introduced into a suitable blending machine and blended together so that the active ingredient is adsorbed on the inert carrier material. It is optional in this case that a small volume of a suitable organic solvent is added in order to accelerate uniform blending. Thereafter, a solution of the binder is added and thoroughly mixed or, alternatively, a binder in a powdery form is added and mixed together followed by the admixture of a solvent for the binder to continue blending. The thus obtained mixture of the active

ingredient, inert carrier, binder and, optionally, stabilizer is then granulated into granules or balls having an average diameter of 0.3 to 10 mm by use of a suitable granulator and the like machine. The solvent for the binder can preferably  
5    ably dissolve also the active ingredient since otherwise a drawback may be caused that the active ingredient is isolated on the surface of the particles.

    The particles or spherical bodies containing the active  
10    ingredient are then provided with a coating film of the film-forming polymeric material. optionally, admixed with an inorganic powdery material. The method for coating is well known in the art including (a) a method in which the solid particles are brought into a fluidized state and a solution  
15    of the film-forming polymeric material, optionally, containing the inorganic powdery material in suspension is sprayed onto the particles and (b) a method in which the solid particles are admixed with a solution of the film-forming polymeric material followed by the admixture of the inorganic  
20    powdery material and dividing of the mixture into a particulate form which is then dried in a fluidized state, if necessary.

    In the above mentioned method (a), the coating procedure on the fluidized particles should preferably be conducted under control of the temperature, for example, in the  
25    range from 5 to 50 °C since a higher temperature may cause

an increased vaporization loss of the active ingredient while a lower temperature is undesirable due to the extremely slow evaporation of the solvent to cause sticking of the particles together without giving a uniform coating. It is  
5 noted that the solvent for the film-forming polymeric material should have a boiling point of 120 °C or below because the velocity of evaporation of a solvent boiling above 120 °C is too low so that frequent sticking of the particles is caused which can be avoided only by increasing the temperature of the base particles above 50 °C with the sacrifice of  
10 the increased vaporization loss of the active ingredient.

The concentration of the film-forming polymeric material in the solution under spraying on to the base particles  
15 is preferably in the range from 0.5 to 10 % by weight and the solution may contain the inorganic powdery material in suspension in an amount within the above described limit. The addition of the inorganic powdery material is advantageous not only in the easiness in the control of the rate of  
20 vapor emission from the finished vapor-releasing body but also in the prevention of sticking of the particles together in the course of the spray coating to improve the uniformity of coating and in the possibility of decreasing the temperature of the particles under the procedure of coating. Similar advantages are obtained by the admixture of the inorganic  
25 powdery material also in the method (b) described above.

As a modification of the spray coating of the core particles, it is optional that the particles are suspended or dispersed in a solution of the film-forming polymeric material and the dispersion or suspension is spray-dried to form  
5 dried particles coated with the film of the film-forming polymeric material.

The coating amount of the film-forming polymeric material such as the cellulose derivatives on the solid base  
10 particles should usually be in the range from 5 to 70 % by weight based on the weight of the base particles. The emission velocity of the gasifiable and diffusible active substance from the inventive sustainedly vapor-releasing body can be controlled in a wide range by suitably selecting various  
15 parameters such as the weight proportion of the gasifiable and diffusible active substance and the inert carrier material, surface area of the base particles, type of the film-forming polymeric material, thickness of the coating film formed of the film-forming polymeric material and the  
20 like.

In the following, the sustainedly vapor-releasing body of the present invention is described in more detail by way of examples.

25  
Example 1.

Spherical or cylindrical base beads of about 1 mm

diameter were prepared of a uniform blend composed of 30 parts by weight of a light anhydrous silicic acid (Aerosil, a product by Nippon Aerosil Co.) and 30 parts by weight of cis-11-tetradecenyl acetate known as a sex pheromone of a  
5 noxious insect "tea toatrix" with admixture of 2.0 parts by weight of a hydroxypropyl cellulose (HPC, a product by Shin-Etsu Chemical Co.) as a binder and 180 parts by weight of ethyl alcohol as a wetting agent by use of a conventional extrusion type apparatus for beads preparation.

10

After drying, the thus prepared base beads were provided with a coating film of a hydroxypropyl methyl cellulose phthalate (HP-55, a product by Shin-Etsu Chemical Co.) in a coating amount of 30 % by weight based on the base beads by  
15 spraying a 6 % solution of the cellulose derivative in a 8:2 by weight mixture of ethyl alcohol and water by use of a fluidizing coater.

The content of the active ingredient cis-11-tetradecenyl acetate in the thus coated beads was determined by disintegrating the beads and extracting the ingredient in acetone and analyzing the acetone extract by the gas chromatography using methyl laurate as an internal standard to give a result of 36.7 % by weight based on the amount of the coated  
20 beads. The rate of emission of the active ingredient from the thus coated beads was examined by keeping 270 mg of the coated beads containing about 100 mg of the active  
25

ingredient under an air flow of 0.5 m/second at 30 °C and periodically determining the weight decrease along with the gas chromatographic analysis of the ingredient to give the results shown in Table 1 below indicating the remaining  
5 amount of the pheromone compound in mg after keeping the beads up to 70 days under the above mentioned conditions.

As is understood from this table, the emission rate of the pheromone compound was approximately constant at about  
10 2.1 mg/day during the first 40 days and the remaining amount of the pheromone compound after 60 days was only 5 % or smaller of the initial impregnation indicating that the coated beads here prepared were quite satisfactory as a sustainedly vapor-releasing body for an insectan sex pheromone.

15 Stability of the coated beads against water was examined by dipping the beads in water at 30 °C for 10 days to find no noticeable changes in the appearance of the beads and in the pheromone compound contained therein indicating  
20 the high stability of the coated beads against water.

#### Example 2.

The procedures for the preparation of the base beads containing cis-11-tetradecenyl acetate and coating thereof  
25 with hydroxypropyl methylcellulose phthalate were substantially the same as in Example 1 except that the coating amount of the cellulose derivative was 50 % by weight based

on the base beads. The analysis of the coated beads undertaken in the same manner as in Example 1 indicated that the content of the pheromone compound therein was 31.5 % by weight.

5

The test of the coated beads for the releasing velocity of the pheromone compound was performed in the same manner as in Example 1 taking 320 mg of the coated beads at the start. The decrease of the pheromone content in the lapse of time was as shown in Table 1 over 70 days of exposure to air. The releasing rate of the pheromone compound was approximately constant and about 1.5 mg/day for the first 50 days.

15

T a b l e 1

Days of atmospheric exposure of beads	Remaining amount of pheromone, mg			
	Example 1	Example 2	Example 4	Example 5
0	100	100	100	100
10	75	81	66	75
20	55	65	42	56
30	33	52	24	40
40	17	38	14	28
50	8	25	7	18
60	3	15	2	10
70	1	9		6

Comparison of the results obtained in Examples 1 and 2 indicates that the releasing velocity of the pheromone from the coated beads can be controlled by suitably selecting the coating amount on the base beads.

5

Example 3.

A uniform blend of a light anhydrous silicic acid and cis-11-tetradecenyl acetate in equal amounts was subjected to granulation and coating in a fluidizing apparatus by spraying a 5 % by weight solution of a cellulose acetate (L-20, a product by Dai-cel Chemical Co.) in a 9:1 by weight mixture of methylene chloride and ethyl alcohol. The average particle diameter of the granules was about 0.4 mm and the coating amount of the cellulose acetate was 45 % by weight based on the base granules.

15

The thus prepared granules were disintegrated in and extracted with acetone and the acetone extract was analyzed by the gas chromatography to find that the content of cis-11-tetradecenyl acetate in the granules was 23 % by weight. The tests for the velocity of pheromone emission from the granules and the stability of the granules against water gave substantially the same results as in Example 1.

20

25 Example 4.

Base beads of spherical and cylindrical forms having an average diameter of 1 mm were prepared by granulating in an

extrusion granulator a uniform blend prepared by mixing 30 parts by weight of a light anhydrous silicic acid, 3 parts by weight of a stabilizer for pheromone compounds and 30 parts by weight of a 1:1 by weight mixture of cis-11-hexadecenyl acetate and cis-11-hexadecenyl aldehyde followed by the addition of 180 parts by weight of a 5 % solution of the same cellulose acetate as used in Example 3 in a 9:1 by weight mixture of methylene chloride and ethyl alcohol as a binder.

10

The thus prepared base beads were provided with a coating film of an ethylcellulose (Ethocell Standard, a product by Dow Chemical Co.) in a coating amount of 20 % by weight based on the base beads by spraying a 6 % solution of the ethylcellulose in a 8:2 by weight mixture of ethyl alcohol and toluene in a fluidizing coater with warm air at 45 °C as the fluidizing medium. The analysis of the thus finished coated beads gave the results that the contents of cis-11-hexadecenyl acetate and cis-11-hexadecenyl aldehyde in the beads were 17.2 % by weight and 17.0 % by weight, respectively, to give a total content of the pheromone compounds of 34.2 % by weight indicating that the loss of the pheromone compounds was negligibly small by the evaporation or denaturation in the course of the preparation of the base beads and coating.

25

The coated beads were subjected to the test of the

releasing velocity of the pheromone compounds in the same manner as in Example 1 taking 292 mg of the beads at the start. The results obtained by the determination of the remaining amount of the pheromone compounds were as shown in Table 1.

Example 5.

The procedures for the preparation of the base beads and the coating thereof with the ethylcellulose were the same as in Example 4 except that the coating amount of the ethylcellulose was 40 % by weight based on the base beads. The analysis of the coated beads gave the results that the contents of cis-11-hexadecenyl acetate and cis-11-hexadecenyl aldehyde were 14.6 % by weight and 14.5 % by weight, respectively, to give a total content of the pheromone compounds of 29.1 % by weight. The coated beads were subjected to the test of the releasing velocity of the pheromone compounds in the same manner as in Example 1 to give the results shown in Table 1. The results obtained in Examples 4 and 5 leads to a conclusion that the pheromone-containing coated beads according to the invention are quite satisfactory in the sustained vapor releasability of the pheromone compounds.

Examples 6 to 9.

Substantially the same procedures for the preparation of the base beads and coating thereof as in Example 1 were

performed with varied combinations of the types and amounts of the pheromone compounds, stabilizer for the pheromone compounds, inert carrier materials, binders, and film-forming polymeric materials as indicated in Table 2 below in which the content of each of the components is given in % by weight. The pheromone-containing coated beads prepared in each of the Examples were quite satisfactory in respect of the sustained releasability of the pheromone vapor.

10 In Table 2, the names of the pheromone compounds, the binder materials and the film-forming polymeric materials were abridged as follows.

(Pheromone compounds)

15 Z-11-TDA: cis-11-tetradecenyl acetate  
Z-11-HDA: cis-11-hexadecenyl acetate  
Z-11-HDAL: cis-11-hexadecenyl aldehyde  
Z-7-ECN: cis-7-eicosen-11-one  
Z-8-DDA: cis-8-dodecenyl acetate

(Binders and film-forming polymeric materials)

20 HPMC: hydroxypropyl methylcellulose  
EC: ethylcellulose  
CA: cellulose acetate  
PVA: polyvinyl alcohol

25 Example 10.

Substantially the same procedures for the preparation of the base beads and coating thereof as in Example 1 were

Table 2

Example No.	6	7	8	9
5 Pheromone compound (%)	Z-7-ECN (52)	Z-8-DDA (21)	Z-11-TDA (13)	Z-11-HDA (9.5) Z-11-HDAL (9.5)
Stabilizer of pheromone, %	3.5	0	0	1.9
Inert carrier, (%)	Anhydrous silicic acid (28)	Calcium carbonate (49)	Crystalline cellulose (37)	Anhydrous silicic acid (20)
10 Binder (%)	PVA (4.5)	Starch (18)	HPMC (21)	CA (15)
Film-forming polymeric material (%)	CA (12)	Pullulan (12)	Polyacrylic acid derivative (29)	EC (44)
15 Average particle diameter of finished particles, mm	3.1	3.1	1.1	0.7

undertaken except that the coating liquid used in this case was a suspension of 6 parts by weight of talc in 100 parts by weight of a 6 % solution of the same hydroxypropyl methylcellulose in a 8:2 by weight mixture of ethyl alcohol and water and the temperature of the fluidizing air was 35 °C instead of 45 °C. The coating amount of the mixture of the cellulose derivative and talc was 40 % by weight based on the base beads. The coating procedure could be performed with no troubles of sticking together of the beads at all.

Analysis of the thus obtained pheromone-containing coated beads gave a result that the content of the pheromone compound in the beads was 34.6 % by weight indicating that almost no loss of the compound had taken place by evaporation in the course of the processing.

The coated beads were subjected to the test of the releasing velocity of of pheromone compound in the same manner as in Example 1 by taking 290 mg of the beads at the start to give the results shown in Table 3, from which it was concluded that the releasing velocity of the pheromone was approximately constant and 2.8 mg/day for the first 25 days and the remaining amount of the compound after lapse of 50 days was only about 5 % so that the coated beads were very satisfactory in respect of the well controlled releasing velocity and the extremely small eventually remaining and unutilizable amount of the pheromone compound.

#### Example 11.

The same procedures for the preparation of the base beads and coating thereof as in the preceding example were performed except that the coating amount was 66 % by weight based on the base beads. The content of cis-11-tetradecenyl acetate in the thus obtained coated beads determined by the gas chromatographic analysis was 29.1 % by weight.

The coated beads were subjected to the test of the

releasing velocity of the pheromone compound in the same manner as in Example 1 by taking 345 mg of the beads at the start to give the results shown in Table 3.

5 Example 12.

Substantially the same procedures for the preparation of the base beads and coating thereof as in Example 10 were performed except that the suspension of talc as a coating liquid was prepared by dispersing 2 parts by weight of the talc in 100 parts by weight of the 6 % solution of the same cellulose derivative in the same solvent mixture and the temperature of the fluidizing air was 39 °C instead of 45 °C. The coating amount was 50 % by weight based on the base beads. The content of cis-11-tetradecenyl acetate in the thus prepared coated beads was 32.0 % by weight.

The pheromone-containing coated beads obtained as above were subjected to the test of the releasing velocity of the pheromone compound in the same manner as in Example 1 by taking 310 mg of the beads at the start to give the results shown in Table 3 below, from which it is clear that the releasing velocity in this case is somewhat lower than in Examples 10 and 11 indicating good controllability of the releasing velocity by the formulation and amount of coating.

25

Example 13.

Fifty parts by weight of the base beads prepared in

T a b l e 3

	Days of atmo- spheric exposure of beads	Remaining amount of pheromone, mg		
		Example 10	Example 11	Example 12
5	0	100	100	100
	10	64	76	80
	20	39	53	61
	30	22	37	44
10	40	12	24	32
	50	6	16	22
	60		10	14
	70			7

15 Example 10 were mixed with 65 parts by weight of a 20 % so-  
 lution of a hydroxypropyl methylcellulose phthalate in a 8:2  
 by weight mixture of ethyl alcohol and water and then with  
 50 parts by weight of talc followed by dividing into gran-  
 ules and drying by fluidization with warm air at 40 °C as  
 20 the fluidizing medium. The analysis of the thus obtained  
 pheromone-containing coated granules performed in the same  
 manner as in Example 1 gave a result that the content of the  
 pheromone compound therein was 21.2 % by weight of cis-11-  
 tetradecenyl acetate indicating substantial absence of the  
 25 evaporation loss of the compound during the processing.

Examples 14 to 17.

Substantially the same procedures for the preparation of the base beads and coating as in Example 1 were performed with varied combinations of the types and amounts of the pheromone compounds, stabilizers of pheromone compounds, inert carriers, binders, film-forming polymeric materials and inorganic powdery materials in the coating film as indicated in Table 4 below. The thus prepared pheromone-containing coated beads in each of the Examples were quite satisfactory as a sustainedly vapor releasing body of the pheromone compound.

The abridgements in Table 4 for the names of the pheromone compounds, binders and film-forming polymeric materials are the same as in Table 2.

Example 18.

A bead product containing an organophosphorus insecticide and coated with the hydroxypropyl cellulose was prepared in substantially the same manner and formulation as in Example 1 excepting the replacement of cis-11-tetradecenyl acetate with the same amount of an insecticide diazinon. The coating amount of the hydroxypropyl cellulose was 32 % by weight. After 30 days of atmospheric exposure under the same conditions as in Example 1, 42 % of the insecticide remained in the beads indicating a quite satisfactory behavior of sustained vapor-releasing.

T a b l e 4

Example No.	14	15	16	17
5 Pheromone compound (%)	Z-11-HDA (12) Z-11-HDAL (12)	Z-7-ECN (48)	Z-8-DDA (18)	Z-11-TDA (12)
Stabilizer of pheromone, %	2.5	3.5	0	0
Inert carrier, (%)	Anhydrous silicic acid (25)	Anhydrous silicic acid (24)	Calcium carbonate (40)	Crystalline cellulose (34)
10 Binder (%)	CA (19)	PVA (4.5)	Starch (16)	HPMC (20)
Film-forming polymeric material (%)	EC (20)	CA (15)	Pullulan (17)	Polyacrylic acid derivative (20)
Inorganic powder (%)	Talc (10)	Sodium silicate (15)	Talc (9)	Calcium carbonate (15)
15 Average particle diameter of finished particles, mm	1.2	3.2	3.1	1.3

## Example 19.

20 A bead product containing naphthalene and coated with the hydroxypropyl cellulose was prepared in substantially the same manner and formulation as in Example 1 excepting the replacement of cis-11-tetradecenyl acetate with the same amount of naphthalene. The coating amount of the hydroxy-

25 propyl cellulose was 45 % by weight. After 15 days of the atmospheric exposure under the same conditions as in Example 1, 48 % of the naphthalene remained in the beads indicating a

quite satisfactory behavior of sustained vapor-releasing.

Example 20.

Perfume-containing beads of spherical and cylindrical  
5 forms having an average diameter of 1 mm were prepared in  
substantially the same manner as in Example 4 excepting the  
replacement of the insectan pheromone compounds with the  
same amount of  $\alpha$ -limonene. Coating of the base beads was  
performed in the same manner as in Example 4 with the same  
10 ethylcellulose excepting that the concentration of the  
ethylcellulose in the coating solution was 4 % by weight  
instead of 5 % and the coating amount was 30 % by weight  
instead of 20 %.

15 The thus prepared perfume-containing coated beads were  
extracted with acetone and analyzed by gas chromatography  
with methyl laurate as the internal standard to give a re-  
sult that the content of the  $\alpha$ -limonene in the beads was  
32.0 % by weight.

20

The perfume-containing beads were subjected to the test  
of the releasing velocity of the perfume in the same manner  
as in Example 1 by taking 313 mg of the beads at the start  
to give the results shown in Table 5 below.

25

Example 21.

The same procedures for the preparation of the perfume-

containing base beads and coating thereof with ethylcellulose as in the preceding example were performed excepting that the coating amount was 40 % by weight based on the base beads. The analysis of these coated beads gave a result that  
5 the content of  $\alpha$ -limonene therein was 30.1 % by weight. The test of these beads for the releasing velocity of the perfume undertaken in the same manner as in Example 1 by taking 332 mg of the beads at the start gave the results shown in Table 5.

10

Example 22.

The same procedures for the perfume-containing base beads and coating thereof were performed in the same manner as in Example 20 except that 180 parts by weight of the  
15 binder solution contained 10 parts by weight of the same cellulose acetate instead of 5 parts by weight and the coating amount on the base beads with the same ethylcellulose was 40 % by weight. The content of the perfume in the coated beads was 27.0 % by weight as determined by the gas chroma-  
20 tography. The results of the test for the releasing velocity of the perfume from these beads undertaken in the same manner as in the preceding example by taking 370 mg of the coated beads at the start were as shown in Table 5.

25

Comparison of the results in Examples 20 to 22 shown in Table 5 leads to a conclusion that the releasing velocity of the perfume from the coated beads can be controlled by

T a b l e 5

Days of atmospheric exposure of beads	Remaining amount of perfume, mg					
	Example 20	Example 21	Example 22	Example 26	Example 27	Example 28
0	100	100	100	100	100	100
10	55	70	78	65	71	76
20	30	48	57	35	45	52
30	12	28	39	19	27	33
40	5	16	24	9	15	19

modifying the amount of the binder and the coating amount on the beads with the film-forming polymeric material.

#### Comparative Example 1.

Beads of activated alumina having an average diameter of 2 mm were prepared by activating the beads shaped of powdery aluminum hydroxide with a hydroxypropyl methylcellulose (TC-5R, a product by Shin-Etsu Chemical Co.) as the binder and 10 parts by weight of  $\alpha$ -limonene were adsorbed on 30 parts by weight of the beads. The perfume-supporting beads were then subjected to coating by fluidization in the same manner as in Example 20 with a 6 % solution of the same ethylcellulose in a 8:2 by weight mixture of ethyl alcohol and toluene. The chromatographic analysis of the perfume-bearing coated beads gave a result that the content of the  $\alpha$ -limonene therein was only 43 % of the calculated value

indicating a great loss of the perfume by evaporation during processing.

Exmples 23 to 25.

5           Substantially the same procedures for the preparation  
of the perfume-containing base beads and coating thereof  
with a film-forming polymeric material as in Examples 20 to  
22 were performed with varied combinations of the types and  
amounts of the perfumes, inert carriers, binders and film-  
10   forming polymeric materials as indicated in Table 6 below.  
The abridgements of the names of the binders and the film-  
forming polymeric materials are the same as in Tables 2 and  
4 excepting HPC which is for hydroxypropyl cellulose. The  
perfume-containing coated beads prepared in each of the Ex-  
15   amples were quite satisfactory in respect of the sustained  
releasability of the perfume vapor.

Example 26.

20           Substantially the same procedures for the preparation  
of the perfume-containing base beads and coating thereof as  
in Example 20 were performed except that the coating liquid  
used in this case was a suspension of talc in an ethylcellu-  
lose solution prepared by dispersing 4 parts by weight of  
talc in 100 parts by weight of a 4 % solution of the same  
25   ethylcellulose in a 8:2 by weight mixture of ethyl alcohol  
and toluene and the temperature of the fluidizing air in the  
coating procedure was 36 °C insted of 45 °C. The coating

Table 6

Example No.	23	24	25	30	31	32
Perfume (%)	Leaf alcoholtiglate (10)	Leaf alcoholtiglate (51)	Compound lemon perfume (31)	Leaf alcoholtiglate (8.2)	Leaf alcoholtiglate (47)	Compound lemon perfume (34)
Inert carrier, (%)	Crystalline cellulose (40)	Anhydrous sillicic acid (27)	Anhydrous sillicic acid (35)	Crystalline cellulose (36)	Anhydrous sillicic acid (25)	Anhydrous sillicic acid (34)
Binder (%)	PVA (19)	HPC (10)	CA (21)	PVA (17)	HPC (9.4)	CA (10)
Film-forming polymeric material (%)	CA (31)	CA (12)	HPMC (13)	CA (21)	CA (14)	HPMC (11)
Inorganic powder (%)	-	-	-	Talc (18)	Talc (4.6)	Talc (11)
Average particle diameter of finished beads, mm	1.8	3.1	3.1	1.9	3.3	3.1

amount on the base beads was 40 % by weight. The coating procedure could be performed satisfactorily with no troubles of sticking together of the beads at all.

5        The content of  $\alpha$ -limonene in the thus coated beads was 31.0 % by weight as determined by the gas chromatography indicating that almost no evaporation loss took place during the processing. The coated beads were subjected to the test of the rate of vapor releasing of  $\alpha$ -limonene in the same  
10       manner as in Example 1 by taking 323 mg of the coated beads at the start to give the results shown in Table 5.

Example 27.

15       Substantially the same procedures for the preparation of the perfume-containing base beads and coating thereof were undertaken as in the preceding example except that the coating amount on the beads was 65 % by weight instead of 40 % by weight. The content of  $\alpha$ -limonene in the thus coated beads was 26.0 % by weight. The test for the rate of vapor  
20       releasing of the perfume undertaken by taking 385 mg of the coated beads at the start gave the results shown in Table 5.

Example 28.

25       The procedure for the preparation of the perfume-containing base beads was the same as in Example 26 and coating of the base beads was performed with a coating liquid prepared by dispersing and suspending 1.5 parts by weight of

talc in 100 parts by weight of a 4 % solution of the same ethyl cellulose in a 8:2 by weight mixture of ethyl alcohol and toluene at a temperature of 33 °C of the fluidizing air. The coating amount was 50 % by weight on the base beads. The content of  $\alpha$ -limonene in the thus coated beads was 28.4 % by weight. The coated beads were subjected to the test of the releasing velocity of  $\alpha$ -limonene in the same manner as in the preceding example by taking 352 mg of the coated beads at the start to give the results shown in Table 5.

10

Example 29.

Fifty parts by weight of the base beads obtained in Example 26 were admixed with 50 parts by weight of a 25 % by weight aqueous solution of a hydroxypropyl methylcellulose (TC-5R, a product by Shin-Etsu Chemical Co.) and then 40 parts by weight of talc and the blend was divided into granular form followed by drying under fluidization. The content of  $\alpha$ -limonene in the thus prepared beads was 24.6 % by weight as determined by the gas chromatography.

20

Examples 30 to 32.

The procedures for the preparation of perfume-containing base beads and coating thereof were performed in substantially the same manner as in Examples 26 to 28 with varied combinations of the types and amounts of the perfumes, inert carriers, binders, film-forming polymeric materials and inorganic powders as indicated in Table 6 in which the

25

abridge-ments for the binders and the film-forming polymeric materials are the same as in Tables 2 and 4. The perfume-containing beads thus prepared in each of the Examples were quite satisfactory as a sustainedly vapor-releasing body.

WHAT IS CLAIMED IS:

1. A sustainedly vapor-releasing body for emission of a gasifiable and diffusible substance having activity in the atmosphere which comprises a solid base particle comprising the gasifiable and diffusible active substance, an inert carrier material and a binder and a coating layer on the surface of the solid base particle formed of a film-forming composition comprising a film-forming polymeric material.
2. The sustainedly vapor-releasing body as claimed in claim 1 wherein the film-forming composition forming the coating layer on the solid base particle further comprises an inorganic powdery material.
3. The sustainedly vapor-releasing body as claimed in claim 1 wherein the weight ratio of the gasifiable and diffusible active substance to the inert carrier material in the solid base particle is in the range from 1:0.3 to 1:10.
4. The sustainedly vapor-releasing body as claimed in claim 1 wherein the weight ratio of the coating layer to the solid base particle is in the range from 5 to 70 %.
5. The sustainedly vapor-releasing body as claimed in claim 2 wherein the amount of the inorganic powdery material in the coating layer is 4 times by weight or smaller of the

amount of the film-forming polymeric material.

6. The sustainedly vapor-releasing body as claimed in claim 1 wherein the film-forming polymeric material is a solvent-soluble derivative of cellulose.

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# EUROPEAN SEARCH REPORT

**0131783**  
Application number

EP 84 10 7132

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
X	GB-A-2 067 406 (MONTEDISON) * claims *	1,3,4	A 01 N 25/26 A 01 N 25/18 A 61 L 9/04
X	--- GB-A-1 517 410 (S.C. JOHNSON & SON) * page 1, lines 6-39; claims *	1,3,6	
A	--- MANUFACTURING CHEMIST & AEROSOL NEWS, vol. 45, no. 4, April 1974, pages 19-21, London, GB; J.F. PICKARD et al.: "Film coating: 1 Formulation and process considerations" * page 19, centre column, paragraphs 3-5, right-hand column, paragraphs 2,3 *	1,2,6	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 7)
			A 01 N A 61 L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 03-10-1984	Examiner FLETCHER A.S.
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>&amp; : member of the same patent family, corresponding document</p>			